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ART. XIV.—*Manganese Deficiency of Cereals: Plot Experiments and a New Hypothesis.*

By G. W. LEEPER, M.Sc.

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### Introduction.

It is now generally recognized that manganese is an essential element in the growth and reproduction of plants. Oats are especially sensitive to a deficiency of manganese. Barley and wheat are not quite so sensitive, while rye and most of the common grasses are far less sensitive, though not even rye is immune. The actual symptoms of the deficiency are shown in most characteristic fashion by oats, in which the disease has been called "grey-speck." These symptoms have been fully described and illustrated by Samuel and Piper (1928), and by Davies and Jones (1931).

In the last few years, cases of manganese deficiency have been reported from many parts of Europe, North America, and Australia, as occurring on many important crops besides wheat, barley, and oats. This deficiency occurs sometimes on soils that have naturally a neutral or alkaline reaction, as in the cases recorded in Western Australia by Carne (1927), and in South Australia by Samuel and Piper (1928), and sometimes on soils naturally acid in reaction, after so much lime has been added as to make them neutral or alkaline, as in Wales (Davies and Jones, 1931), Rhode Island (Gilbert *et al.*, 1926), Sweden (Arrhenius, 1926), etc. The present case belongs to the second class, and is the first of its kind to be reported in Australia; and though the soil in question does not belong to any type met with in practice, the results obtained show some features of general interest.

### Description of Soil.

The area referred to in this work is a plot of land 21 yards by 9 yards, in the grounds of the Agriculture School of the University of Melbourne. The soil is a grey sandy loam to a depth of 18 inches; below this it rapidly becomes heavier, with occasional lumps of yellow clay, until at 30 inches it passes into an impermeable yellow clay which is derived from the Silurian mudstones of the district.

The surface soil, which is homogeneous in texture and appearance to a depth of 18 inches, has the same origin as the adjacent garden beds of the University grounds; this is a sandy loam which contains about 3 per cent. of gravel (above 2 mm. diameter), in the form of ironstone and quartz grains. The fine earth consists of 32 per cent. of coarse sand (2 to 0.2 mm.) 38 of fine sand (0.2 to 0.02 mm.) 15 of silt (0.02 to 0.002 mm.), 12 of clay (below .002 mm.), and about 3 of organic matter. The coarse sand consists of quartz together with some grains of ironstone. The fine sand contains, besides much quartz, 18 per cent. of plagioclase, 6 per cent. of augite, and other basaltic minerals. This augite is mostly angular, and shows no sign of weathering. It appears that the soil consists of material derived from the nearby basalt country, but not normally weathered. (It has been suggested that it may have been made up from road sweepings derived from the use of basalt as road-metal.) Its natural pH value is 5.0. (This figure, like all other pH values recorded in this paper, refers to a 1:1 soil-water suspension measured with the quinhydrone electrode at 20° C.; where the value of a surface soil is quoted, this refers to the 8 inches of surface soil).

The area under discussion has been cropped fairly continuously with numerous varieties of crops, mainly cereals, since 1914, and is protected from birds by wire netting. It has been heavily limed, and contains about 0.2 per cent.  $\text{CaCO}_3$  in the 9 inches of surface soil; the last liming was a dressing of about 2 tons to the acre in 1923. The effect of this liming has been to bring the pH of the upper 18 inches well into the alkaline range. The reaction of the surface soil varies from 7.2 to 7.7 over the area; this falls to about 7.0 at 18 inches, then 6.5 from 18 to 30 inches, and then rises again to 8.0 at 40 inches, where the heavy clay occurs. It may be remarked that the disease discussed here does not seem to occur on soil derived directly from the Silurian mudstones, even after liming.

## Results of Plot Trials.

### EXPERIMENTS IN 1928\*.

A portion of the area was used in 1928 for various experimental treatments in work carried out by Glynne. For some years previously it had been noted that oats, wheat, and barley had been making poor growth, and it was thought that the sickness of the crops might be due to parasitic organisms in the soil. Sulphur and various sulphur compounds were used, and the treatments comprised varying applications of ammonium sulphate (ranging from 27 to 81 cwt. per acre), sulphur (from

\* In all these experiments the seed was put in during the last ten days of May, and plants were harvested by pulling up in the last fifteen days of December.

6 to 20 cwt. per acre), sulphuric acid (from 1 ton to 3 tons), sodium thiosulphate crystals (from 17 to 75 cwt.), calcium carbonate (from 1 to 3 tons), and various combinations of these last three substances. These tests were replicated over 44 plots each one yard square, on ground that had grown partly wheat and partly oats in the previous season. The plots were sown with Federation wheat, 4 rows per plot. Superphosphate, which had been applied at 2 cwt. per acre for some years past, was omitted this year.

The season of 1928 was a dry one, and the crop was an almost complete failure on all but nine of the plots. These successful plots included the heavier treatments with sulphur (13 cwt. or more) and sulphuric acid (2 tons or more) and the lightest treatment with ammonium sulphate (27 cwt.) The heavier treatments with ammonium sulphate, and all the thiosulphate treatments, were evidently toxic.

The pH values of the 8 inches of surface soil of various plots were determined in December, 1928. It is shown in Table I. that all plots of pH more alkaline than 6.7 were failures irrespective of treatment; but while all the control plots, of pH from 7.4 to 7.7, failed to produce any grain worth mentioning, the nine plots that produced grain had pH values ranging from 5.5 to 6.6, with yields of from 5.3 to 30.3 bushels per acre.

TABLE I.—FEDERATION WHEAT, 1928.

Treatment.	Number of Plots.	Yield, bushels per acre.	
		Average.	Maximum Yield.
All thiosulphates and heavier amm. sulph. .. ..	12	Nil (Toxic)	0.0
All treatments and controls, pH 6.7-7.7 .. ..	11	0.4	1.7
Various treatments, pH 6.0-6.6 .. ..	6	14.2	26.2
Various treatments, pH < 6.0 .. ..	3	22.5	29.9

Rainfall, May to November inclusive, 9.65 inches.

No evidence of parasitical attack was found on the control plots, and in her account of the work Glynne (1929) suggested that there was an actual deficiency of sulphur in the soil; but this suggestion cannot be right, as the sulphate sulphur in the surface soil of the control plots is 0.01 per cent., enough for many successive crops.

## EXPERIMENTS IN 1929.

In 1929 the same plots were resown with Federation wheat on the same lines, with 2 cwt. per acre superphosphate, but no further treatment. Yields were far better this year, but in spite of high variability among the control plots, the correlation of good yield with low pH was again very noticeable. Control plots ranged from 8.5 to 33.4 bushels, while acidic plots and those previously treated with thiosulphate gave yields ranging from 14.1 to 56.2 bushels. The results are summarized in Table II., where thiosulphate treatments are collected in one group, irrespective of pH. It is remarkable that the best yields on the acidic plots were on those of pH more acid than 6.3. The heavy applications of ammonium sulphate have brought down the pH to 6.7 or less.

TABLE II.—FEDERATION WHEAT AFTER WHEAT, 1929.

Treatment.	Plots.	pH.	Yield, bushels per acre.	
			Average.	Maximum.
All thiosulphates ..	10	6.6-7.6	28.1	56.0
Excluding thiosulphates—				
All below pH 7.0 ..	7	5.6-7.0	34.0	52.3
Intermediate ..	4	7.0-7.2	25.2	32.5
All above pH 7.2 ..	23	7.2-7.8	16.9	33.2

Rainfall, May to November inclusive, 13.99 inches.

## EXPERIMENTS IN 1930.

It was thought that the effect of sulphur might have been connected with the intake of nitrogen or phosphorus. A fresh experiment was therefore carried out in 1930, in which the treatments included, beside a 1-ton per acre dressing of sulphur, a 2-cwt. dressing of sodium nitrate and a 4-cwt. dressing of superphosphate. These three treatments were replicated four times each, and with four control plots this gave a total of sixteen plots each of 2 square yards. Free Gallipoli wheat was sown on adjacent soil that had been fallowed the previous year and had accumulated large reserves of nitrate. Most of the nitrate was washed away by heavy rain in early May (before sowing), but there was an ample supply left in all plots; the nitrate nitrogen in the surface soil (0.9 in.) averaged 36 lb. per acre at sowing (May 25), 15 lb. at the end of July, and then fell to a steady value of about 5 lb. through September and October. The nitrate concentration of the various plots during June and July was correlated with the tiller count made on September 19; but when the harvest was taken in December, there was no



correlation between autumn or winter nitrate and yield. Nitrate concentration was also unconnected with the use of sulphur or superphosphate. The application of superphosphate had no effect on tillering nor on the final yield; this is not surprising in view of the heavy doses given in former years. But the correlation of final yield with pH was as marked as in previous years. The sulphur oxidized quickly in the autumn and lowered the pH (determined on a composite of six cores), from 7.3-7.6 to 6.3-6.6 within six weeks after application. It would seem that the bacteria responsible for this oxidation are somewhat sensitive to the acidity which they produce, as even in December a considerable amount of sulphur remained unchanged, especially around the roots of the plants. A similar effect has been noted by Rountree (1933) at Renmark. One of the unsulphured plots in this experiment had a consistent acidic reaction, about 6.6. It is not known how this occurred, but this plot is included with the four sulphured plots in Table III., leaving eleven alkaline plots with which to compare the acidic plots. (This seems reasonable since in their whole behaviour the plants on this exceptional plot followed those on the sulphured plots). The high production of tillers per plant is due to the fact that the rows were spaced at an interval of 2 feet.

TABLE III.—FREE GALLIPOLI WHEAT AFTER FALLOW, 1930.

—	No. of Plots.	pH.	Tillers.		Ears.		Grain.		
			Per Plant	Per square yard.	Per square yard.	Per cent. surviving.	Gram per ear.	Bushels per acre.	
								Average.	Range.
Alkaline plots	11	7.2-7.6	5.3	208	126	61	0.69	15.5	10.8-18.8
Acidic plots	5	6.4-6.7	4.8	186	<b>147</b>	<b>79</b>	<b>0.86</b>	<b>22.6</b>	20.2-25.3

Standard error of difference of mean, 1.3 bushels per acre.  
 Rainfall, May to November, 15.30 inches.  
 Yields significantly different from controls are in black type.

## EXPERIMENTS IN 1931.

It had by now seemed likely that the trouble was manganese deficiency, and further tests were then carried out with this in mind. It is known that the good effects of sulphur on certain soils are connected with the flocculating effect of the calcium sulphate that is formed, so a 1-ton gypsum treatment—enough to give a marked flocculation—was included in 1931. Other treatments were 40 lb. each of “chemically pure” crystalline hydrates of  $\text{CuSO}_4$ ,  $\text{FeSO}_4$ ,  $\text{MnSO}_4$ , and  $\text{Ca}(\text{MnO}_4)_2$ ; and sulphur at 30 cwt. per acre. Each treatment was replicated over four plots of 1 square yard each. Free Gallipoli wheat was

sown in rows at intervals of 1 foot, with 2 cwt. superphosphate and 2 cwt. calcium nitrate on all plots. Tillers were counted as before in late September, and these showed a mean value of 2.6 per plant, no treatment showing any significant difference from any other. Neither gypsum nor any other salt applied showed any significant difference from the control plots at harvest. Treatments other than sulphur are therefore not entered separately in Table IV., which compares the four sulphured plots with (a) the four control plots, and (b) sixteen alkaline plots of various treatments, chosen from those neighbouring the sulphured plots.

TABLE IV.—FREE GALLIPOLI WHEAT AFTER OATS AND BARLEY, 1931.

—	No. of Plots.	pH.	Tillers.		Ears.		Grain.		
			Per Plant.	Per square yard.	Per square yard.	Per cent. surviving.	Gram per ear.	Bushels per acre.	
								Mean.	Range.
Alkaline plots (control) ..	4	7.3-7.6	2.69	210	133	63	0.61	14.7	8.9-19.7
Alkaline plots (various) ..	16	7.2-7.7	2.58	214	120	56	0.67	14.3	3.0-34.8
Acidic plots	4	6.3-6.5	2.50	206	141	68	<b>0.92</b>	<b>23.5</b>	18.7-29.3

Standard error of mean of 4 plots, 2.76 bushels per acre.

Rainfall, May to November, 17.26 inches.

Yields significantly different from controls are in black.

The result was similar to that of 1930. Yields on control and other alkaline plots were very erratic, although the alkalinity was nowhere greater than pH 7.7 nor less than pH 7.2.

On one patch of soil in this test the disease hardly showed itself, so that a sulphured plot in this section could not gain much advantage over the control, while on another patch the sulphured plot gave a yield of 128 gm. to the square yard, where surrounding alkaline plots averaged only 29 gm. This characteristically high variability of the soil with respect to manganese deficiency was partially eliminated from the calculation of the standard error, by Fisher and Wishart's (1930) method of analysis of total variance. The figures, however, underestimate the true effect of the sulphur.

The manganese used in this test was applied at the rate of 10 lb. Mn per acre, in four plots each as  $\text{Ca}(\text{MnO}_4)_2$  and  $\text{MnSO}_4$  at germination and in four more plots as  $\text{MnSO}_4$  in early September. It is remarkable that this addition to the soil of about 100 times as much manganese as the crop needed had no perceptible effect on the development of the plant. Chemical analyses at harvest time showed that these plants had taken up no more manganese than the controls. Other tests done on this soil, together with results reported elsewhere by Samuel and

Piper (1928), indicate that at least 30 lb. per acre of soluble manganese applied at sowing to the soil may be needed if such severe deficiency is to be overcome by a surface application. Many disappointing results of the surface application of manganese salts have been due to the use of too small quantities. For example, Turner and Findlay (1932) in Yorkshire attempted to control the disease with 45 lb. per acre of  $MnSO_4$  crystals, sprayed over the crop. This was successful to a limited extent, but only if done after the disease had appeared—i.e., the manganese was then absorbed through the leaf, and not through the soil and root.

## EXPERIMENTS IN 1932.

Since the deficiency is confined to soils of pH above about 6.7, there are two possible ways of overcoming the unfavourable state of the soil in the field. The soil may be left alkaline and enough manganese be added, preferably as sulphate, to carry the plant through the season, or the reaction of the soil may be permanently changed by the addition of sulphur or any other acidifying agent—a line of action that is feasible only when the  $CaCO_3$  in the soil is fairly low, as here. The literature to date contains no comparisons of the effects of these two treatments on the development of the plant. With this comparison in view, therefore, a fresh experiment was carried out in 1932.

In this year Free Gallipoli wheat was sown with 2 cwt. each superphosphate and calcium nitrate; treatments comprised sulphur (1 ton per acre),  $MnSO_4$  crystals at germination (1 cwt. and 3 cwt.) and in early September (1 cwt.). Each treatment was replicated four times in square-yard plots, and four control plots were included. The original pH of about 7.5 was brought down by the sulphur only to 6.8-7.0, a figure not low enough to ensure a uniform cure of the deficiency; however, some definite conclusions may be drawn from the results which are summarized in Table V.

TABLE V.—FREE GALLIPOLI WHEAT AFTER WHEAT, 1932.

	No. of Plots.	Tillers.		Ears.		Grain.		
		Per Plant.	Per square yard.	Per square yard.	Per cent. surviving.	Gram per ear.	Bushels per acre.	
							Mean.	Range.
Control ..	4	2.93	253	130	51	0.98	22.5	11.2-38.9
Sulphur ..	4	3.37	259	<b>188</b>	<b>72</b>	<b>1.33</b>	<b>44.2</b>	30.2-59.0
$MnSO_4$ —								
1 cwt. (autumn)	4	<b>3.62</b>	<b>303</b>	<b>211</b>	<b>70</b>	<b>1.41</b>	<b>53.0</b>	35.5-78.6
1 cwt. (spring)	4	3.06	259	<b>167</b>	<b>64</b>	1.06	31.3	18.5-39.1
3 cwt. (autumn)	4	<b>3.54</b>	<b>280</b>	<b>176</b>	<b>63</b>	1.17	36.5	20.6-48.0

Standard error of mean of four plots, 7.1 bushels per acre.

Rainfall, May to November, 13.44 inches.

Yields significantly different from controls are in black.

These figures are not as significant as one would desire. For instance, the figure of 53 bushels quoted for 1 cwt.  $MnSO_4$  includes an individual plot of 78.6 bushels. The sulphur was not applied heavily enough to control the disease uniformly, and the application of  $MnSO_4$  to the surface soil after germination also failed to give complete or uniform control. It has been shown by Scott (1932) at Corny Point, South Australia, that manganese applied with the seed, like superphosphate, gives the plant a better chance of overcoming the deficiency than when applied to the surface after germination; 28 lb. of the hydrated crystals used in this way were more effective than 112 lb. applied to the surface soil.

#### EXPERIMENTS IN 1933.

The experiment was therefore continued in 1933 on the same plots. Superphosphate, 2 cwt. per acre, was applied with the seed, but no nitrogenous fertilizer was added. Sulphur was again applied, and an extra 10 cwt. per acre now brought the pH to the desired range (6.2-6.5). The plots given  $MnSO_4$  late in 1932 were now given  $MnSO_4$  sown with the seed, those given 3 cwt. in 1932 were given 1 cwt. applied to the soil after germination, while those given 1 cwt. early in 1932 were left without further manganese in order to determine if there were any residual effect. Results are summarized in Table VI.

TABLE VI.—FREE GALLIOLI WHEAT AFTER WHEAT, 1933.

—	No. of Plots.	Tillers.		Ears.		Grain.		
		Per Plant.	Per square yard.	Per square yard.	Per cent. surviving.	Gram per ear.	Bushels per acre.	
							Mean.	Range.
Control ..	4	2.23	196	54	27	0.66	6.3	1.1-9.8
Sulphur ..	4	2.47	194	<b>123</b>	<b>66*</b>	<b>1.30*</b>	<b>29.4*</b>	22.6-39.6
$MnSO_4$ —								
With seed ..	4	<b>2.75</b>	<b>251</b>	<b>119</b>	<b>47</b>	<b>0.82</b>	<b>17.4</b>	9.1-26.8
After germination ..	4	2.47	216	<b>100</b>	<b>46</b>	<b>0.93</b>	<b>16.5</b>	9.8-24.7
Residual ..	4	2.46	218	84	<b>39</b>	<b>0.85</b>	12.8	3.1-21.2

Standard error of mean of four plots, 2.39 bushels per acre.

Rainfall, May to November, 13.53 inches.

Yields significantly different from control are in black. Yields significantly the highest in their respective columns are asterisked.

This season was definitely less favourable than the preceding, and in addition the soil was poor in available nitrogen; the nitrate nitrogen in the top 9 inches of soil at sowing averaged eight parts per million on the alkaline plots and four on the sulphured, acidic plots. When the results of the various years were compared, it was seen that there is a very marked dependence on the weather, as is shown by the complete failure of

alkaline plots in the dry season 1928 as compared with 15-bushel yields in the better years 1930 and 1931, and 22.5 bushels in the excellent season 1932, in which the distribution of rainfall was very favourable. It has, in fact, often been noted that manganese deficiency is more marked in a dry year than in a wet one.

### Review of Results from Experimental Plots.

While the results reported here are largely confirmatory of previous work, they have peculiar features which in spite of the artificial nature of the soil may have a bearing on the problem in other countries. Some of these are as follows:—

1. *Tillering*.—In each of four years 1930 to 1933, the number of tillers per square yard, counted in late September, was unaffected by sulphur, although the leaves of plants on acidic soil were a darker green. On the other hand, germination was rather adversely affected by sulphur in 1933; and both in 1930 and still more in 1933, the plants on the acidic plots were definitely yellower and poorer in appearance than those on the control, or other alkaline plots, up till the end of August. In 1933 this was correlated with a lower accumulation of nitrate on the acidic soil during the preceding summer and autumn, though it is doubtful if this alone explains the effects noted.

Manganese sulphate, on the other hand, increases the tillering somewhat if it is applied early enough and copiously enough to the soil. If it is applied in the most efficient way—with the seed—it is shown in Table VI. to have a very favourable effect on tillering.

2. *Survival of Tillers to Ears*.—The survival of tillers to ears is much improved by either sulphur or manganese, but in the less favourable year 1933 sulphur was far more effective in this respect. In every year there is a very striking relative improvement of the sulphured plots during October and November, and they show their superiority in every way at harvest.

3. *Size of Ears*.—While the total number of ears is much increased by either treatment, the ears on the sulphured plots gave far more grain than those sown with  $MnSO_4$  in 1933. Analysis shows that this superiority exists in both mean number of spikelets per ear, mean number of grains per spikelet, and weight per grain.

Sterility is more marked on the alkaline plots; representative samples from these in 1931 showed that on the average 41 per cent. of the spikelets were sterile, compared with 32 per cent. on the acidic plots. Both grains per spikelet and weight per



grain are also higher on the acidic plots—all of which illustrates the importance of manganese for the development of flower and fruit.

The course of the disease seems to vary a good deal according to climate and soil; while in Melbourne the plants on "deficient" soil appear fairly healthy through winter and sicken only when the soil begins to dry in spring, in Western Australia (Carne, 1927) the plants appear to recover in spring after looking poor in August; this recovery by plants that have shown "grey speck" in September has also been observed on inadequately sulphured plots in Melbourne, and is probably connected with mild cases of deficiency only. Odland and Crandall (1932) in Rhode Island found deficiency showing in some years on the spring crops and not on the autumn, and vice versa in other years.

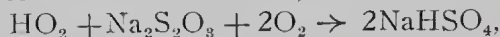
4. *Residual Effect of MnSO<sub>4</sub>*.—The effect of heavy application of MnSO<sub>4</sub> a year earlier is still seen in a somewhat healthier growth, but is strikingly small.

5. *Effect of Heavy Applications of MnSO<sub>4</sub>*.—The comparative failure in 1932 of the crop on soil given 3 cwt. per acre of MnSO<sub>4</sub> crystals is striking; however, the yield is not significantly lower than that of the 1 cwt. plots, and the difference only shows how variable the soil is with regard to the deficiency-effect. (See manganese content of grain, below.)

6. *Effect of Nitrates*.—Nitrates are said to make the disease worse. In this work, the deficiency has been more marked on plots of higher nitrate status, both in 1930 and in 1933.

7. *Effect of Ammonium Salts*.—Ammonium sulphate has been recommended on grounds of economy for grey-speck in countries of northern Europe, notably by Arrhenius (1926) in dealing with lime-induced grey-speck on podzolic sands in south-western Sweden. Its good effect is clearly related to its acidifying action, though it is hard to see how it could be as efficient in the small amounts used (2 cwt.) as is sulphur in large doses. In the work reported here, the amounts of ammonium sulphate used in 1928 (Table I.) were so huge as to lower the pH to a point where manganese is available; the effect seems to have nothing to do with the amount of soluble nitrogen in the soil, which in 1930 was no higher on the ammonium sulphate plots of 1928 than on the controls, although the treated plots were very much healthier.

8. *Effect of Thiosulphates*.—Thiosulphates are oxidized in the soil according to the ultimate scheme,



but in many plots the fall in alkalinity due to the NaHSO<sub>4</sub> produced was not very marked; in fact, the best plot in 1929, yielding at the rate of 56 bushels per acre, after a 75-cwt. dose of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.5H<sub>2</sub>O in early 1928, had a pH in bulk sample

(surface 8 inches) of 7.3. It is possible that there was a local production of high enough acidity to overcome the deficiency. Otherwise, the highly reducing nature of the thiosulphate ion may have been responsible for the effect noted. (This will be discussed later.)

9. *pH Value of Profile.*—The pH of the soil falls to 6.5 at 18 inches. At such a value one would expect a fair availability of manganese, and the failure of a wheat plant to collect its necessary fraction of a milligram from this level may be partly due to the fact that it is essential for the manganese to be at hand from the earliest stages of growth. (However, spraying  $MnSO_4$  solution on very sick oat plants growing on this soil, in early September, led in about a week to a recovery from an apparently hopeless position, and finally these plants yielded reasonable amounts of grain.) But a plant already suffering from deficiency would not be likely to explore the 18-inch level at all thoroughly.

10. *Varietal Differences.*—It has often been noted that different varieties show very different degrees of tolerance (e.g., Davies and Jones, 1931). This effect was very marked in this work also, from observations on varieties of wheat, barley, and oats which were grown in connexion with other work. Common wheat was found to be less sensitive than emmer and macaroni, while single varieties of spelt and "mummy" were about as tolerant of deficiency as most varieties of common wheat. Barley is generally more tolerant than oats, but the most tolerant oat varieties (viz., Lachlan, and still more Palestine) are better than some barley varieties (such as Gatami and Hännchen). But there are many oat varieties which are so sensitive that they may die in September, an extreme case being Dawn (a local variety), though others such as Fulghum and Algerian are also very sensitive. Of the barleys, Pryor and Moira are the least sensitive.

11.—*Manganese in Dry Matter and Requirements of Various Plants.*—The total manganese in the dry matter of a plant is closely connected with its availability in the soil. The manganese content of healthy plants of wheat, oats, and barley ranges from 15 to over 200 parts per million (p.p.m.) of dry matter; a figure of less than 15 p.p.m. indicates a probable deficiency. The difference in sensitiveness of various plants to this deficiency has already been remarked on; it is very striking to see how invariably rye yields a splendid crop while the neighbouring row of oats or wheat is languishing. Wimmera rye-grass (*Lolium subulatum*) and wild vetches (*Vicia sativa*) also grow vigorously to maturity on this soil, which is evidently highly fertile for all but sensitive plants. In fact, weeds of all kinds have been observed to flourish; and during the autumn of 1934 it was observed that alkaline plots of the previous year's experiments

were supporting a vigorous growth of weeds, largely *Sonchus oleraceus*, *Malva rotundifolia*, and *Portulaca oleracea*, while the acidic plots were almost bare. This avoidance of acidic plots may have been due to the direct effect of the sulphur, in lowering the pH, causing a very high concentration of  $\text{CaSO}_4$ , or producing other unfavourable oxidation products. It was incidentally noted in 1930 that the activity of *Azotobacter* was adversely affected by sulphuring. These facts may be compared with the poor growth shown also by wheat on the acidic soil up till late in August. Rye, rye-grass, and the tolerant barley variety Pryor, were sampled in the spring of 1931 and the whole plants were analyzed for manganese. It was found in each case that the total manganese was only 10 to 11 p.p.m. of dry matter. It would appear, therefore, in accordance with Samuel and Piper's work on culture solutions, that tolerance implies a lower need for manganese, rather than a greater power to obtain it, though no doubt plants differ in this power also; of course, the total Mn in the crop of the tolerant plant may be considerable. The question is bound up with that of the function of manganese, about which very little is known as yet.

TABLE VII.—MANGANESE IN GRAIN OF WHEAT.

Treatment.	Sample.	Year.	Yield of oven-dry grain at selected point, grams per square yard.	Mn parts per million dry matter.	Mn in grain.	
					Milli-grams per square yard.	Grams per acre.
Control (alkaline) ..	1	1930	77	12	0.92	4.5
	2	1930	59	8	0.47	2.3
	3	1931	73	9	0.66	3.2
	4	1932	65	12	0.78	3.8
	5	1932	39	10	0.39	1.9
	6	1933	50	5.5	0.28	1.3
$\text{MnSO}_4$ in autumn ..	7	1931	69	10	0.69	3.3
	8	1932	440	12	5.28	25.6
	9	1932	189	30	5.67	27.5
	10	1933	45	12	0.54	2.6
	11	1933	135	32	4.33	2.1
Sulphur (acidic) ..	12	1930	103	21	2.16	10.5
	13	1932	119	7	0.83	4.5
	14	1932	324	27	8.75	42.5
	15	1933	136	32	4.35	21.1

The figures collected in Table VII. refer only to the grain of Free Gallipoli wheat. The table shows, firstly, that the manganese content of grain from alkaline, deficient soil (samples 1 to 6) ranges from 5.5 to 12 p.p.m., the yields being mainly poor. Of samples 7 to 11, from soil to which  $\text{MnSO}_4$  had been applied, Nos. 8, 9, and 11 showed a marked response to the

applied manganese. The low proportion of manganese in the grain of the enormous crop of No. 8 is striking; however, the total Mn removed by the crop is quite high. Information is not available about the Mn in the straw. Samples 7 and 10 showed symptoms of Mn deficiency, and both the yield and the Mn content are of the same order as in the control plots—in each case the added  $\text{MnSO}_4$  was presumably precipitated out of reach of the main mass of roots. Sample 10 was collected from soil that had been treated with 3 cwt. per acre of  $\text{MnSO}_4$  crystals; it gives clear evidence that the comparative failure of these 3-cwt. plot was connected with very low local availability of added manganese. Samples 12, 14, and 15 show the typical increase in concentration in Mn that follows acidification. Sample 13 was taken from an inadequately sulphured patch of pH 7.0, where the yield was disappointing and symptoms of deficiency were seen. The figure 7 p.p.m. again recalls the alkaline plots.

### General Discussion of Availability of Manganese in Soil.

These experiments make it of interest to review the question of the availability of manganese in the soil. The nature of this availability has been discussed by several workers, a useful summary being given by Piper (1931). Work in South Australia has made it clear that figures for the total manganese in the soil (above a certain minimum), or for strong or dilute acid extracts, have little or no bearing on the problem; a healthy soil may well yield less soluble manganese to an extracting acid than will a deficient soil (Samuel and Piper, 1928). Soils more acid than pH 6.7 do not show the disease. On such soils manganese compounds do no good, and on more definitely acidic soils they may be harmful. On the alkaline side of this boundary line (especially beyond pH 7.0) the manganous ion may be represented by the bicarbonate, by exchangeable manganese, or by basic compounds (phosphate, carbonate, silicate) which as Britton (1930) showed, begin to appear as bulky precipitates below pH 7. The existence of such basic compounds makes it irrelevant in this regard to quote the laboratory precipitation of manganous hydroxide from chloride solutions at pH 8 to 9. It is probably safe to say, however, that exchangeable manganese is the only important store of the bivalent ion available in alkaline soils of any considerable degree of maturity.

At pH values above 7, bivalent manganese is easily oxidized in the air to a higher valence. The composition of this manganic material is not constant, but it may be conventionally written as the dioxide,  $\text{MnO}_2$ . Piper showed that water-soluble manganese (as  $\text{MnSO}_4$ ) was largely converted\* into the "dioxide" within

\* His method, however, as is shown later in this paper, is bound to underestimate the extent of this conversion (Piper, 1931, p. 766).



three weeks when it was added to a soil of high pH, whether deficient or not, at a water content well below saturation. As the dioxide is practically insoluble it follows that soluble manganese compounds, when added to a soil of high pH, will be precipitated at the surface even more effectively than other elements (such as potassium) which are held by the soil only in the form of exchangeable bases. The failure of light applications of  $MnSO_4$  to overcome manganese deficiency may be explained by the complete precipitation of manganese in the surface inch of soil, which can be reached by only a small proportion of the root system, i.e., the failure is positional, not physiological. This aspect of availability is discussed in general by Spencer and Stewart (1934). This concentration of manganese in the surface soil under certain conditions was well shown by Bishop (1928), who found that the surface soil at a depth of 3 inches under a Eucalyptus tree contained 3 to 7 per cent. Mn, derived from the leaves, twigs, and bark, while the subsoil, and the surface soil away from the tree, contained 0.25 to 0.6 per cent. Mn.

#### PREVIOUS HYPOTHESES.

The scheme put forward by Piper may be summarized as follows:—Manganese is absorbed only as the bivalent ion, and  $MnO_2$  is unavailable. While at low pH values Mn exists in solution in fair concentration, it exists at high pH only as the bivalent exchangeable base or as insoluble dioxide. There is an equilibrium between these forms, swinging towards the exchangeable form as conditions favour reduction, and towards the dioxide as conditions favour oxidation. The occurrence of deficiency on neutral and alkaline soils must therefore depend on the oxidation-reduction potential ( $E_h$ ) of the soil.

Under fully aerobic conditions, the effect of the very low solubility of the manganic compounds would be to reduce the maximum possible concentration of manganous ions in equilibrium with the atmosphere to a very low figure, especially if bacteria were also oxidizing manganous to manganic compounds.

Steenbjerg (1933) accepts the same explanation as Piper. He discusses the prevalence of the disease on light, sandy soils, and concludes (p. 428), "The content of available manganese in the soil is controlled by (1) the reaction, and (2) the oxidation-reduction conditions."

This hypothesis is supported by the fact that some manganese present in soils as  $MnO_2$  may be brought back into solution by reducing conditions; this may be connected with the good effects of thiosulphate referred to earlier in this paper, but is best shown by waterlogging, especially in the presence of a source of bacterial energy such as glucose. Piper used for many of his tests the



deficient soil that occurs locally around Mount Gambier (S. Aust.). This soil type has been described by Prescott and Piper (1931); it is a highly immature volcanic ash, containing variable quantities of  $\text{CaCO}_3$ . The University soil appears to be, in fact, a synthetic imitation of the Mount Gambier soil, being light, permeable, calcareous, well-drained, and highly immature, with an abundance of primary minerals such as augite in the fine sand, and of good fertility except for the manganese deficiency. The similarity extends also to the very low availability of added  $\text{MnSO}_4$ . For the effect of waterlogging, Piper compared a sample from Mount Gambier, of pH 7.4, with a sample from the experimental fields at the Waite Institute, Glen Osmond—a red-brown earth, also of pH 7.4, on which no sign of manganese deficiency had been observed. These soils were waterlogged under various conditions for three weeks; in every case the water-soluble manganese was increased by this treatment, though the healthy soil yielded always more than the deficient soil. In all cases pot tests showed that deficient soils, after a long enough waterlogging, became free from deficiency during the following few months at least, and possibly for much longer.

It is thus implied that healthy soils of high pH either have a lower oxidation-reduction potential, or are capable of developing one more easily, than deficient soils. It is, of course, conceivable that even a well-drained soil on account of natural heterogeneity might contain numerous tiny waterlogged patches in which the dioxide might be reduced. However, the following facts show that this explanation cannot be right.

#### EXPERIMENTS ON WATERLOGGING.

The alkaline "deficient" University soil, sampled to 8 inches, was compared with the sulphured, healthy soil from neighbouring plots, and with the surface soil from Doon, in the Wimmera district of Victoria. This soil is typical of the so-called "Wimmera Black" soil. It is a grey self-mulching clay, slightly calcareous and of pH 7.3; it produces good crops of wheat in a normal season, and the dry matter of the crop contains 90 p.p.m. of manganese.

Samples of the deficient (alkaline) and of the healthy (sulphured) University soil, and of the Doon soil, were waterlogged at laboratory temperatures (about  $10^\circ \text{C.}$ ) both with and without the addition of 0.25 per cent. of their weight of glucose, and at the end of three weeks were shaken for an hour with enough water to bring the soil:water ration to 1:5, and filtered through candle filters. This was the method used by Piper, whose figures for the Mount Gambier and Glen Osmond soils are also included in Table VIII. for comparison, though doubtless the temperature of waterlogging was considerably higher in his experiments.

TABLE VIII.—AMOUNTS OF MANGANESE MADE WATER-SOLUBLE BY THREE WEEKS' WATERLOGGING.

(Parts per million.)

	University Soil.		Dooen.	Mount Gambier.	Glen Osmond.
	Alkaline.	Sulphured.			
Waterlogged without glucose ..	0.08	2.8	0.02	1.2	6.3
Waterlogged with 0.25 per cent. glucose .. .. .	2.5	11.8	2.6	5.4	13.0

It will be seen that the waterlogging has brought manganese into solution in greatest amounts in the Glen Osmond and healthy (sulphured) University soils; but the equally healthy Dooen soil has yielded less soluble manganese than the two deficient soils studied. In another experiment on the Dooen soil not a trace was found. The waterlogging with glucose shows a similar order of results.

Even under intensely reducing conditions the Dooen soil cannot produce manganous ions for the soil solution. But, in fact, the Dooen soil is more actively *oxidizing* than the deficient University soil. This was shown by shaking each soil with solutions of benzidine and of guaiacum, which are turned blue by actively oxidizing soils. The Dooen soil gave a good colour with each reagent, while the University soil gave no colour. This test will be seen to support the suggestion put forward later in this paper.

#### EXPERIMENTS WITH LEACHING REAGENTS.

Piper also found that the Mount Gambier soil yielded only 4.2 p.p.m. of soluble manganese to rapid leaching with cold 0.05N sulphuric acid, while the healthy Glen Osmond soil yielded 65.7 p.p.m. Further leaching with the same acid containing 0.2 per cent. quinol in each case dissolved relatively huge amounts of manganese, presumably from the state of  $MnO_2$  (again using this formula in a conventional way). This supports his idea that a deficient soil contains only small quantities of exchangeable manganese, while it may be rich in the dioxide.

The same extracting method was therefore tried on both deficient (alkaline) and healthy (sulphured) soil from the University plots, and also on alkaline soil to which manganese sulphate had been added. In each case 30 gm. samples of air-dry soil were leached first with 500 c.c. of 0.05N  $H_2SO_4$ , then with 500 c.c. of 0.05N  $H_2SO_4$  containing 1 gm. quinol in solution.

TABLE IX.—AMOUNTS OF MANGANESE DISSOLVED FROM SOILS BY LEACHING WITH VARIOUS REAGENTS.

(Parts per million.)

(a) Without quinol. (b) With 0.2 per cent. quinol.

Soil.	pH.	Dissolved by 0.05N H <sub>2</sub> SO <sub>4</sub> .		Dissolved by ammonium acetate pH 4.6.		Dissolved by ammonium acetate pH 7.0.		Total soluble in conc. HCl.
		(a)	(b)	(a)	(b)	(a)	(b)	
Glen Osmond .. ..	7.4*	66*	315*	..	..	..	..	260*
Mount Gambier .. ..	7.4*	4*	124*	7.5	18	0.2	3.7	324*
University alkaline .. ..	7.3	34	11	12	..	1	11	160
+ 30 parts per million Mn .. ..	7.3	50	23	..	..	3	39	..
University sulphured .. ..	6.1	44	11	..	..	5	13	..
Dooen .. ..	7.3	97	166	10	170	Tr.	137	370
Tatchera sand .. ..	8.6	40	..	40	..	3.6	154	..
Penola .. ..	6.9*	0	<1	..	..	Tr.	0.4	50*
Corn Point .. ..	8.0*	3	8	..	..	2.6	8.0	187*

\* These figures are taken from Piper (1931), and Samuel and Piper (1928).

Piper's figures for Glen Osmond and Mount Gambier are also included for comparison in Table IX.

It will be seen that in spite of the mineralogical and physical similarities of the soils from the University and from Mount Gambier, the results here reported seem incompatible with the theory discussed at the beginning of this section. There is little significant difference in acid-soluble manganese between deficient and healthy samples of University soil and the healthy Glen Osmond soil; but the most striking fact about the sulphuric acid extracts is the very low figure for the "dioxide" values (quinol-soluble manganese) of the former.

Further tests were therefore made by leaching 30 gm. of soil with 500 c.c. of a normal solution of ammonium acetate at pH 7.0, followed by further leaching of the residual soil with the same solution containing 0.2 per cent. quinol. In a few cases additional tests were made in which the solution at pH 7.0 was replaced by a solution of ammonium acetate and acetic acid, of pH 4.6, normal with respect to total acetate. In each case the soil was first warmed to 50° with 100 c.c. of the leaching solution, then cooled and filtered under gentle suction, using successive portions of 50 c.c. of the leaching solution at room temperature. The whole 500 c.c. took about seven hours to filter.

Ammonium acetate was chosen partly for its buffer capacity as emphasized by Schollenberger and Dreibellis, who proposed its use (1928), and partly because it can be completely destroyed in the leachate, so making it possible to use small amounts of liquid for estimating the very small quantities of manganese sometimes present. In spite of these advantages, Steenbjerg

(1933) has shown that ammonium is much less efficient than calcium or magnesium in replacing manganese from alkaline soil. However, the differences between various soils found in this work would almost certainly reappear with other leaching agents so long as the pH of leaching were standardized.

Table IX. summarizes the results, together with Piper's figures already referred to. The soils tested included the above-mentioned soils, and also the following:—

(1) A sample of Tatchera sand, a Mallee soil, from Tresco (Vic.). This soil has been described by Taylor *et al.* (1933). It has a pH of 8.6, and is perhaps representative of the lighter soils of the Victorian Mallee. Manganese deficiency has never yet been found on such a soil.

(2) A heavy clay from Penola (S. Aust.). This is a reclaimed swamp, of pH 6.9, is highly deficient, and has been experimented on by Piper (1931).

(3) A grey highly calcareous soil from Corny Point (S. Aust.), of pH 8.0. This represents about 10,000 acres of deficient country, and work has been reported on it by Piper and by Scott (1932).

Comparison of results for manganese replaced at various pH values shows how quickly this is repressed by growing alkalinity, until at pH 7 the figures are all small, especially for the Dooen soil, for which not a trace of manganese could be detected. The figures for the "dioxide" manganese, however, show a huge contrast between the deficient and healthy soils; the former have very little at pH 7, the latter have a copious supply at all pH values. Since the pH value of the soil solution in the alkaline and calcareous soils here compared would seldom fall much below 7.0, it would appear that the secret of the success of the Wimmera soil is connected with the presence, not of exchangeable manganese, but of *active* manganese dioxide, which can be easily reduced at a high pH value. The Dooen soil contains more than twelve times as much of this component as does the "deficient" soil from the University. This may explain the results obtained with benzidine and with guaiacum, referred to above.

While healthy alkaline soils *may* be higher in manganese set free by waterlogging (e.g., Glen Osmond) or exchangeable at pH 7.0 (e.g., Tatchera sand), than are deficient soils, these tests fail for the Dooen soil. There is only one respect in which all healthy and deficient soils of high pH are distinguished—viz., in their content of active "dioxide" which is brought into solution by 0.2 per cent. quinol in normal ammonium acetate at pH 7.0. It appears, therefore, that quinol is a chemical metaphor for the plant roots in much the same style as has been suggested for dilute citric acid in the problem of phosphate

availability. This can happen only in one or both of two ways; reducing conditions may be set up at the surface of the root providing a direct source of manganous ions from the more active dioxide, or else colloidal manganic oxide, such as readily oxidizes quinol, can be directly absorbed by the plant. In favour of the former possibility, one may quote the observation of Schreiner, Sullivan, and Reid (1910), that selenites may be reduced to selenium on the surface of a root—a reaction that calls for a higher reducing power at pH 7 than the reduction of manganese dioxide. The possibility of colloidal absorption is not generally favoured, though Comber (1922) has argued in its favour, and work on the water-soluble phosphate of soils points to it (Parker and Pierre, 1928), while the very considerable intake of silica into grasses and cereals growing on soils of pH 5 or less may well be colloidal. Such colloidal material, however, would seem to be a "second choice," being less available than ordinary ions, and therefore needing to be present in fairly copious amount to avoid a deficiency. In either case, one must dispense with the belief in an intermediate condition of manganous ions in the soil solution, especially in view of the failure of the Doon soil to produce more than a trace of soluble manganese under a waterlogging far more drastic than would occur in the field even in a wet winter (since the drainage of this soil is good.)

The success of  $\text{KMnO}_4$  in curing manganese deficiency in some cases (Gilbert *et al.* 1926; Samuel and Piper, 1928) may also be explained if it is the most active form of "manganese dioxide" which prevents deficiency at high pH values.  $\text{KMnO}_4$  can only *increase* the oxidation-reduction potential, so could only do harm if that were the important factor. However, this salt must change very quickly to a bulky mass of colloidal  $\text{MnO}_2$ , which is probably very easily available. Reports on the success of applications of  $\text{MnO}_2$  as such are conflicting, probably because the physical state of the  $\text{MnO}_2$  is so important.

It is interesting to note that apparently only two cases have been reported of manganese deficiency occurring on soils of basaltic or similar origin—namely, the two highly immature soils from Mt. Gambier and the University. Evidently the slow supply of manganese coming from the rich reserve of primary minerals is not enough for the purpose.

### Oxidizing Power of Manganic Compounds.

It is well known that rising alkalinity increases the power of solutions of given strength of either  $\text{Fe}^{++}$  or  $\text{Mn}^{++}$  to reduce many oxidizing agents such as oxygen. The interaction with oxygen is clearly seen in the rapid deepening in colour of ferrous and manganous hydroxides as soon as they are precipitated. The prior formation of an actual basic precipitate of



the bivalent form is not necessary to this oxidation, since ammoniacal solutions of  $\text{MnSO}_4$ , if exposed to the air, show a rapid separation of a manganic deposit, while all but strongly acidic solutions of  $\text{FeSO}_4$  are similarly attacked. In each case this effect is due to the very low solubility of the hydroxide of the more highly oxidized ion. The oxidation-reduction potential ( $E_1$ ) at  $30^\circ\text{C}$ . of an inert electrode dipping into a solution containing ferric and ferrous ions in molar concentrations per liter,  $[\text{Fe}^{+++}]$  and  $[\text{Fe}^{++}]$  respectively, is given by (1), where the low concentrations considered may be taken as equal to activities:—

$$E_1 = 0.74 + 0.06 \log \frac{[\text{Fe}^{+++}]}{[\text{Fe}^{++}]} \quad \dots \quad \dots \quad \dots \quad (1)$$

If the solution is in equilibrium with solid  $\text{Fe}(\text{OH})_3$  (which might well be the case at pH greater than 3) one can combine this formula with the solubility product of  $\text{Fe}(\text{OH})_3$ , namely:—

$$[\text{Fe}^{+++}] \cdot [\text{OH}^-]^3 = 10^{-36},$$

or multiplying by  $[\text{H}^+]^3$ , and using the relation  $[\text{H}^+]^3 \cdot [\text{OH}^-]^3 = 10^{-42}$ ,

$$[\text{Fe}^{+++}] = 10^6 [\text{H}^+]^3$$

(1) now becomes—

$$\begin{aligned} E_1 &= 0.74 + 0.06 \log \frac{10^6 [\text{H}^+]^3}{[\text{Fe}^{++}]} \\ &= 0.74 + 0.36 - 0.18 \text{ pH} - 0.06 \log [\text{Fe}^{++}] \end{aligned}$$

One may arbitrarily fix  $[\text{Fe}^{++}]$  at  $10^{-5}$  (about 0.5 parts per million of soil solution), since it is unlikely to exceed such a figure. If  $[\text{Fe}^{++}]$  is thus considered constant, this gives:—

$$E_1 = 1.40 - 0.18 \text{ pH} \quad \dots \quad \dots \quad \dots \quad (2)$$

This great fall in oxidation potential with rising pH is due to the removal of ferric ion in an insoluble form; a similar fall may be obtained without a change in pH by the addition of ions such as  $\text{F}^-$  or  $\text{C}_2\text{O}_4^{--}$ , which form stable complexes with  $\text{Fe}^{+++}$  and so again remove it from the system. In such a case, ferrous salts can reduce cupric salts, as described by Müller (1908).

In the case of manganese, the potential for a solution in contact with solid  $\text{MnO}_2$  is given different values by different workers; as the accurate value is of minor importance in this argument, we may use the value given by Latimer and Hildebrand (1929):—

$$E_2 = 1.33 + 0.03 \log \frac{[\text{H}^+]^4}{[\text{Mn}^{++}]} \quad \dots \quad \dots \quad \dots \quad (3)$$

Keeping  $[\text{Mn}^{++}]$  constant at  $10^{-5}$ , this gives

$$E_2 = 1.48 - 0.12 \text{ pH} \quad \dots \quad \dots \quad \dots \quad (4)$$

The rate of fall of potential with rising pH is three times (for iron) and twice (for manganese) the rate of 0.06 volts per pH shown by the oxygen, quinhydrone, and hydrogen electrodes. It follows therefore that the compounds  $\text{Fe}(\text{OH})_3$  and  $\text{MnO}_2$  are much stronger oxidizing agents and so more easily reduced, in an acid than in a neutral environment. The importance of this fact (illustrated in Fig. 1) has not been realized enough by soil scientists, although the use of excess acid to prevent or destroy any  $\text{MnO}_2$  precipitate has long been a commonplace of titrations involving  $\text{KMnO}_4$  and oxalates. Very strong acidification raises  $\text{MnO}_2$  into the region of oxygen overvoltage—solutions in fairly strong  $\text{H}_2\text{SO}_4$ , for instance, slowly evolve oxygen on standing.

The use of the term rH is convenient here. This may be taken (for 30° C.) as the thirtieth part of the difference in millivolts between the system considered and the normal hydrogen electrode at the same pH; the rH value of the system  $\text{MnO}_2 - \text{Mn}^{++}$  at pH 0 from (4) would be 49.3; and at pH 7 it would be 35.3. The iron system would have  $\text{rH} = 34.3$  at pH 3, and 18.3 at pH 7—i.e., a fall of two and four rH units, respectively, for every rise of one pH unit.

As yet, little is known of the factors controlling the  $E_h$  (oxidation-reduction potential) and the rH of soils. Heintze, however, has shown (1934) that the soils which she studied lie in a range of rH just above the quinhydrone system, and this rH seems to be independent of pH. However, it must be emphasized that in so far as the potential is set by the system ( $\text{Mn}^{++}$ , sat.  $\text{MnO}_2$ ), it should give a lower rH on liming and a higher rH on acidification.

This point was excellently brought out by Sen-Gupta (1925), who measured the amount of phenol which was destroyed by rapid oxidation when it was added to various soils which had been brought to a low pH value by previous treatment with an acid, followed by a leaching out of the free acid. It was shown conclusively that this oxidizing power of soils depended on their content of  $\text{MnO}_2$ ;  $\text{Fe}_2(\text{SO}_4)_3$  was only very feebly active. This power could be destroyed by mineral acids stronger than 4.5 N, especially by concentrated HCl—i.e., the conditions where  $\text{MnO}_2$  has its highest rH, so is most easily destroyed. So long as this limit was not exceeded, the stronger the acid treatment the better the destruction of the phenol. It was also found that the power of the soil to destroy phenol was removed by treatment with citric or tartaric acid. These acids, being strongly reducing, can dissolve  $\text{MnO}_2$ , being themselves oxidized in the process; working on the manganiferous soils of Hawaii, Dean and Dean (1929) noticed that citric acid was largely destroyed by the active  $\text{MnO}_2$  that was present, so that citric acid extractions for phosphate were often useless.

But if the pH of the soil was raised to the alkaline range (by washing with alkali), phenol was no longer destroyed; re-acidifying largely restored the power to oxidize phenol rapidly. There must obviously have been a big difference in pH values between the alkali-treated and the acid-treated samples—probably enough to change the gap of oxidation-reduction potential between soil and phenol by 300 to 400 millivolts or 10 to 13 rH units; the actual pH figures, however, were apparently not measured.

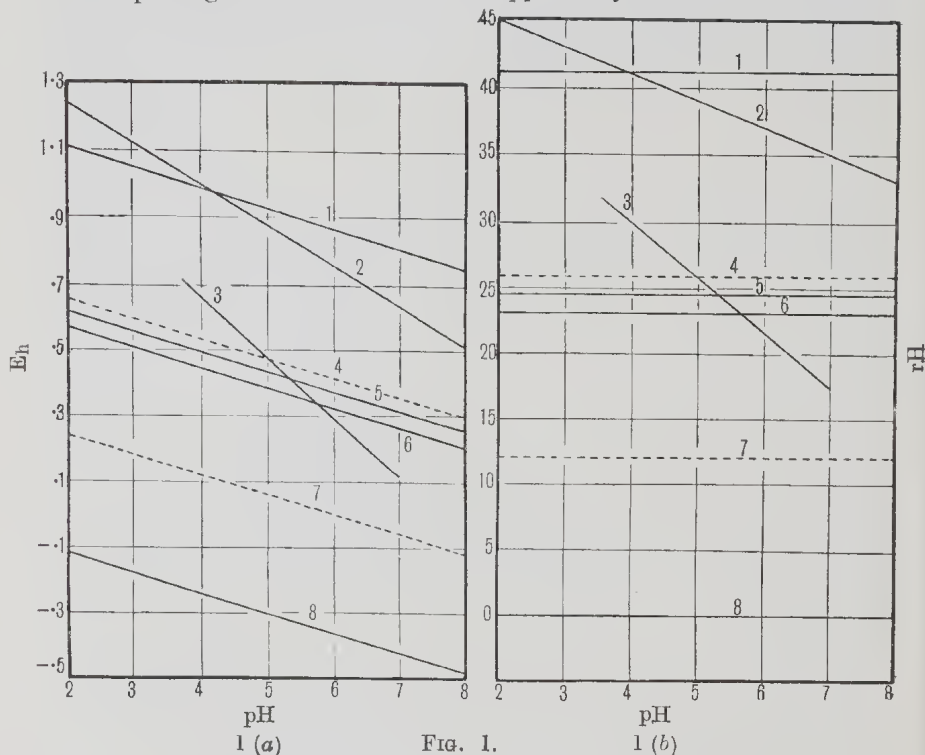


FIG. 1.—1 (a)  $E_h$  values, and 1 (b), rH values, of various systems, numbered as follows:—

1.  $O_2 + 4H^+ + 4e = 2H_2O$
2.  $MnO_2 + 4H^+ + 2e = Mn^{++} (10^{-5}M) + 2H_2O$
3.  $Fe(OH)_3 + 3H^+ + e = Fe^{++} (10^{-5}M) + 3H_2O$
4. Normal Soil
5.  $H_2SeO_3 + 4H^+ + 4e = Se + 3H_2O$
6.  $C_6H_4O_2 + 2H^+ + 2e = C_6H_6O_2$
7. Waterlogged Soil
8.  $2H^+ + 2e = H_2$

Most of Sen-Gupta's tests were made on soil that was treated with acid for 20 minutes, then washed free of acid and tested with the phenol. If the acid was allowed to stand on the soil

for some days, the phenol-destroying power of the soil gradually decreased. It seems very likely that during this period the organic matter of the soil gradually reduced the  $\text{MnO}_2$ —an effect that would be impossible at the pH found in the field, on account of the very different gap of oxidation-reduction potential between  $\text{MnO}_2$  and organic matter at the two pH values of about 1–2 and 6–7 respectively. Soils rich in organic matter were less active than others; this may have been due to the absence of much  $\text{MnO}_2$  in the original soil, or to its partial destruction by organic matter on acidifying.

Figs. 1 (a) and 1 (b) represent graphically the main issues in this argument. 1 (a) shows the actual difference in potential ( $E_h$ ) between the various systems and the normal hydrogen electrode, while 1 (b) shows the same systems reduced to the rH scale, on which the value for the hydrogen electrode at all pH values is taken as zero. The systems ( $\text{Mn}^{++}$ ,  $\text{MnO}_2$ ) and ( $\text{Fe}^{++}$ ,  $\text{Fe}(\text{OH})_3$ ) are plotted in each case for an arbitrary concentration of  $10^{-5}$  gm.-ions per liter of the bivalent ion (such as would not be likely to be greatly exceeded) in equilibrium with the solid oxide or hydroxide of higher valence. The absolute level of the  $E_h$  and rH lines must depend on this arbitrary concentration, and incidentally there is no agreement about the normal potential of the former system. However, the object of the graph is to illustrate the smallness of the rH gap between  $\text{MnO}_2$  and normal soils at high pH, as contrasted with the bigger gap between  $\text{MnO}_2$  and normal soils at low pH, and that between  $\text{MnO}_2$  and waterlogged soils at high pH values. The rH of normal soils is a rough average taken from Heintze (1934), while that of waterlogged soils is a similar average taken from Gillespie (1920), who found a fall due to waterlogging of about 13 rH units for the soils under test. It is of course not implied that these potentials of soils necessarily follow a straight-line formula; the lines as drawn are meant to represent the most typical results obtained to date.

### Quinhydrone Drift.

It is known that the pH values of certain soils are hard to measure accurately with the quinhydrone electrode. The potential shows a rapid drift in the direction of increasing alkalinity, amounting to several tenths of a pH unit within a few seconds after adding the quinhydrone. This effect has been studied by several workers, and the information was well summarized by Best (1931), who showed that it is due to "active"  $\text{MnO}_2$ , which rapidly oxidizes the quinol of the quinhydrone. The  $\text{Mn}(\text{OH})_2$  thus produced is an active base, as pointed out by Schollenberger (1928), so that the pH of the suspension steadily rises. Best estimated this "active  $\text{MnO}_2$ " by determining the manganese liberated from the soil by  $0.05\text{N H}_2\text{SO}_4 + 0.2$  per cent. quinol.

It would seem from the soil analyses quoted in Table IX., and from the above account of Sen-Gupta's work, that such a method is liable to lead to too high a figure. It is the  $\text{MnO}_2$  active at the pH of the soil (usually 6 to 7) which is responsible for "quinhydrone drift", and it appears more satisfactory to estimate such  $\text{MnO}_2$  by leaching with a dilute solution of quinol at approximately the actual pH of the soil, as is done, for example, in the neutral ammonium acetate method described above. Sen-Gupta's test of the destruction of phenol is a qualitative test similar to Best's, showing only acid-active  $\text{MnO}_2$ . Other qualitative tests for active  $\text{MnO}_2$  are carried out at the soil's own pH, viz., the blue colour developed with alcoholic guaiacum or with benzidine, and the green colour developed on long standing with KCNS, as was discussed by Brewer and Carr (1926).

The concentrations of  $\text{MnO}_2$  found in healthy alkaline soils in this work are of the order of 0.01 per cent. Mn. This is below the level at which Best found that the quinhydrone electrode was liable to "drift". Hence, one need not expect that all healthy alkaline soils would show a "quinhydrone drift", but it must follow from the hypothesis suggested in this paper that a soil showing such a drift cannot be associated with manganese deficiency. It is interesting to note that of the soils listed by Best, the deficient Mount Gambier soil does not drift, while the healthy Glen Osmond soil does so. Schollenberger (1930) describes how a "drifting" soil lost its power to drift after leaks of natural gas had made it anaerobic, so reducing  $\text{MnO}_2$  to  $\text{Mn}(\text{OH})_2$ .

### Nature of Manganic Compounds (" $\text{MnO}_2$ ") in Soil.

The state of this active manganic material in the soil is not at all clear. It appears that the manganic oxides may form a continuous series, from the most active to the most inert; for convenience, one may separate these oxides into four classes—(a) extremely active, capable of oxidizing quinol at pH 7 and of oxidizing the organic matter of the soil rapidly in sulphuric acid suspension (pH 1.5 to 2); (b) also very active, capable of oxidizing quinol at pH 7, but only slowly attacking organic matter at pH 1.5-2; (c) moderately active, capable of oxidizing quinol at about pH 2 or  $\text{Na}_2\text{S}_2\text{O}_4$  at pH 7 (see Table X. below); and (d) inert (including all the remaining manganic compound). The total Mn of the soil also includes (e) bivalent Mn present in the minerals of sand, silt, and clay.

Best, for instance, (1931), found that a soil from Bundaberg (Queensland), which gave a bad drift with quinhydrone, yielded 0.32 per cent. of manganese to dilute sulphuric acid, and a further 0.27 per cent. on adding quinol or ferrous ammonium sulphate to the sulphuric acid. These two figures would correspond respectively to (a) and to (b) + (c). Sen-Gupta's test for "active



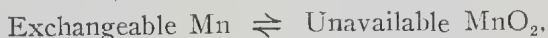
MnO<sub>2</sub>” would also give (b) + (c). Only (a) and (b), however, are concerned in insuring against manganese deficiency, causing “quinhydrone drift”, or reacting with guaiacum.

It is suggested that this difference in activity is to be put in the same category as the “ageing” of colloids. The active fraction (a) is then analogous to the fresh precipitate obtained in the reaction between a permanganate and a manganous salt. Such a precipitate, after thorough washing with 0.05N H<sub>2</sub>SO<sub>4</sub>, when mixed with Mt. Gambier soil (also well leached with the same acid), will give large quantities of Mn to the solution on further leaching with 0.05N H<sub>2</sub>SO<sub>4</sub>. (Probably most normal soils will do the same as Mt. Gambier.) Schollenberger (1928) ascribed the presence of Mn. in a filtrate of a mixture of soil and 0.1N HCl, to the same reduction. The fraction (d) on the other hand is analogous to the most resistant residues of pyrolusite, which dissolve in oxalic and sulphuric acid only after prolonged boiling. In this case, all the fractions are thermodynamically capable of performing the reactions described, but they differ enormously in the speed of reaction.

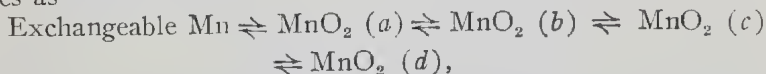
Robinson (1929) and Sen-Gupta (1925) agree that active MnO<sub>2</sub> is present mainly in the coarser fractions. While this statement is no doubt true of the more definitely manganiferous soils, no attempt has been made to test it in the present work with regard to the soils under study; in any case, colloidal activity might well be shown on the surface of the coarser particles.

However, all this discussion assumes that the formula of manganic oxides in the soil is uniformly MnO<sub>2</sub>, whereas in fact there would probably be compounds of every combining proportion from MnO to MnO<sub>2</sub>, which might differ chemically in their oxidizing capacities. In the absence of any information on this matter it is not considered further here.

This separation of MnO<sub>2</sub> into four categories does not rule out the possibility of change from one state to another. Such changes are inevitable in a dynamic system such as soil. The dynamic equilibrium,



of former workers, however, may now be replaced by some such series as—



where it must again be emphasized that the four classes are separated by arbitrary tests. Waterlogging will displace the equilibrium from right to left, as has in fact been shown by Piper (1931). The Dooen soil, for instance, after six weeks' waterlogging, showed a rise of exchangeable Mn from 0 to 8 p.p.m., and of types (a) and (b) together from 137 to 200. The speed of any change in the direction (b) to (c) is quite

unknown. It may well be that the change from (c) to (b) on waterlogging takes place by way of the bivalent ion, but it seems unlikely that this bivalent Mn should escape almost complete oxidation on restoring good drainage.

TABLE X.—AMOUNTS OF MANGANESE DISSOLVED FROM DEFICIENT SOILS BY VARIOUS SUCCESSIVE TREATMENTS. (Parts per Million.)

Soil.	Normal ammonium acetate pH 7.0.				Sulphuric acid + 0.2 per cent. quinol.	
	(i)	(ii)	(iii)	(iv)	$\frac{N}{20}$ acid.	$\frac{N}{2}$ acid.
Mount Gambier .. ..	0.25	3.7	2.0	58	..	..
Penola .. ..	Tr.	0.4	0.0	0.4	0.1	3.5
Corny Point .. ..	2.6	8	n.d.	17	..	..

(i) No reducing agent; (ii) With 0.2 per cent. quinol; (iii) With 0.4 per cent.  $\text{Na}_2\text{SO}_3$ ; (iv) With 0.4 per cent.  $\text{Na}_2\text{S}_2\text{O}_4$ .

Three of the deficient soils studied here were tested successively with more drastic reagents than the solution of 0.2 per cent. quinol at pH 7.0—viz., solutions of 0.4 per cent.  $\text{Na}_2\text{SO}_3$  and 0.4 per cent.  $\text{Na}_2\text{S}_2\text{O}_4$ , in N ammonium acetate, and then with 0.2 per cent. solutions of quinol, first in 0.05N, then in 0.5N  $\text{H}_2\text{SO}_4$ . The results, given in Table X, show the success of  $\text{Na}_2\text{S}_2\text{O}_4$  at pH 7.0 in the case of both Gambier and Corny Point soils. The acid treatment was not tried on the latter as it contains such large amounts of  $\text{CaCO}_3$ ; but in the case of Penola, treatment with 0.5N acid + quinol was needed to dissolve even as much as 1 of the 50 parts of Mn which every million parts of this soil contain. From these figures one might have predicted the results actually obtained by Piper (1931, p. 771) in pot tests—viz., that Penola soil (which has hardly any  $\text{MnO}_2$  of class (c)) would respond more to added Mn than to waterlogging, that the Mt. Gambier soil, with plenty of class (c), would show the best response to waterlogging of the three, while the Corny Point soil would be intermediate.

Figures are included in Table IX, which show that the University soil, to which 30 p.p.m. of Mn had been added in past years as  $\text{MnSO}_4$ , gave almost complete recovery of this extra Mn at pH 7.0. Too much importance must not be given to the exact agreement of these results, on account of the large sampling error; but they do indicate that much of the added  $\text{MnSO}_4$  is held in the soil in a form at least as available as the class (b) above. Yet symptoms of manganese deficiency were observed in the wheat on these plots, and the last two months of growth were disappointing. This fact is provisionally put down to the completeness of precipitation of the Mn in the surface layer of the

soil: the plots in these experiments were not dug (in order to avoid the risk of mixing the soil of neighbouring plots). It is intended to test at a future date how far the response to added  $\text{MnSO}_4$  depends on the thoroughness of mixing of the soil. The chemical analyses quoted above would certainly indicate that a fairly active  $\text{MnO}_2$ , if well mixed with the soil to a depth of several inches, should be quite as effective as any soluble salt of manganese, and 30 p.p.m. of this Mn should ensure against a deficiency. It is clear that manganese brought into the available state by waterlogging must be already intimately mixed with the soil.

While the fairly drastic treatment of waterlogging may be very good for soils which, like that of Mt. Gambier, have large stores of  $\text{MnO}_2$  just below the critical level of availability, it is difficult to see how such a mild reducing agent as well-rotted farm-yard manure could make available to plants any  $\text{MnO}_2$  except such kinds as the plants can in any case secure for themselves. It seems more likely that the good effects sometimes claimed for farm-yard manure are due to its own content of manganese and to its lowering of pH values.

As the pH value of the soil is lowered, more manganese may be leached out, partly, no doubt, by direct reduction of the dioxide and partly because it is easier for exchangeable Mn set free by weathering to accumulate at these more acid levels. The sulphured University soil, for instance (Table IX.), evidently owes its health to the greater concentration of manganese exchangeable at pH 7 and to the greater availability of this manganese at its pH of 6. However, it is not possible from the information available, to determine what importance to ascribe to "exchangeable Mn" which may easily be leached out at low pH levels but cannot be leached at pH 7. The 34 parts of manganese leached by 0.05N acid from the University soil must have come from some other source than the "(a) + (b)"  $\text{MnO}_2$ , which alone could provide only 11 parts. This source might well be a manganous silicate, since the soil is so immature; such a compound might be dissolved at low pH but be quite unavailable at pH 7. It is also interesting to recall the often-noted fact that during the electro-dialysis of soils, manganese is released only in the later stages—i.e., as the pH of the soil drops. This appearance of manganese may be at least partly due to the reduction of  $\text{MnO}_2$ .

It appears that useful information may be obtained about the state of Mn in the various horizons of the soil by the method followed in Table IX.—leaching with buffered solutions at various pH values, containing reducing agents chosen to bring the solution to given rH values.

It is possible that some reagent may be found to replace quinol, which is troublesome to destroy before analyzing extracts for Mn. Meanwhile, it may be noticed that deficient soils contain less than

15 p.p.m. of Mn replaceable by normal ammonium acetate at pH 7.0, including the help of quinol, so that one might guess that a content of, say, 25 to 30 p.p.m. of this manganese was needed to avoid deficiency. No more definite statement can be made with the present figures. In fact, the limit for deficiency probably depends on the climate as well as on the crop.

As the pH of the soil decreases, the life of more active manganese oxides becomes shorter. McGeorge (1923), in discussing the Hawaiian soils that are rich in  $MnO_2$ , says that none has been found with a pH below 5.9. At lower values one would expect the organic matter to reduce the  $MnO_2$  more easily, so that bivalent manganese would be formed and would be washed out.

Since reserves of "active  $MnO_2$ " fall off rapidly with a fall in pH, one might forecast that, other things being equal, it is more dangerous to lime a highly acid than a moderately acid soil. It may be remarked that many of the soils that have become "deficient" after liming have naturally a very acid reaction.

### Effect of Liming.

Steenbjerg (1933) working on field plots, has shown how successive additions of lime to an acid soil quickly lower the amount of manganese replaceable by semi-molar magnesium nitrate. He also estimated the manganese leached in successive portions of 25, 50, or 100 c.c., and showed that while acid soils released most of their total manganese in the first 100 c.c., with alkaline soils this release was much more gradual and prolonged. The difference between these two types is shown in Fig. 2, where the percentage of the total replaceable manganese in the filtrate is plotted against the volume of the filtrate, using Steenbjerg's figures. From the shape of these curves he worked out a function called  $qS$ , which is low for acid soils (curve 1), and high for alkaline soils (curve 2). Steenbjerg concluded that exchangeable manganese was bound in a different and a far firmer way in the alkaline soils; but though this may be true, the differences obtained in the values of  $qS$  must be partly due to the fact that the leaching solutions were unbuffered, so that the first 50 c.c. would be leaching the soil at a much lower pH for acid than for alkaline soils, and so the leaching solution would be more efficient, as shown in Table IX.. Steenbjerg also came to the conclusion (p. 423) that "Other things being equal, of two soils each with the same low figure for total exchangeable Mn, deficiency will be more likely on the soil that has the higher  $qS$  value." One would expect a soil to have a higher  $qS$  value—a slower rate of liberation of Mn—if it had more  $CaCO_3$ ; but it is not clear whether  $CaCO_3$  content is included among the "other things" that are equal.

Whatever may be the importance of this greater firmness of holding of replaceable manganese, it is clear that a great deal of the Mn is oxidized by liming, as is shown by the appearance of black  $\text{MnO}_2$  on the particles of  $\text{CaCO}_3$  (Robinson, 1929), as well as by Piper's experiments quoted on p. 237. The normal decrease in the quantity of Mn available to plants following liming is also shown by Steenbjerg's plant analyses on experimental limed plots, by Mann's work (1930) in laboratory tests, and by Piper's work on the increase of Mn absorbed by plants on acidifying the soil from both Glen Osmond and Mt. Gambier.

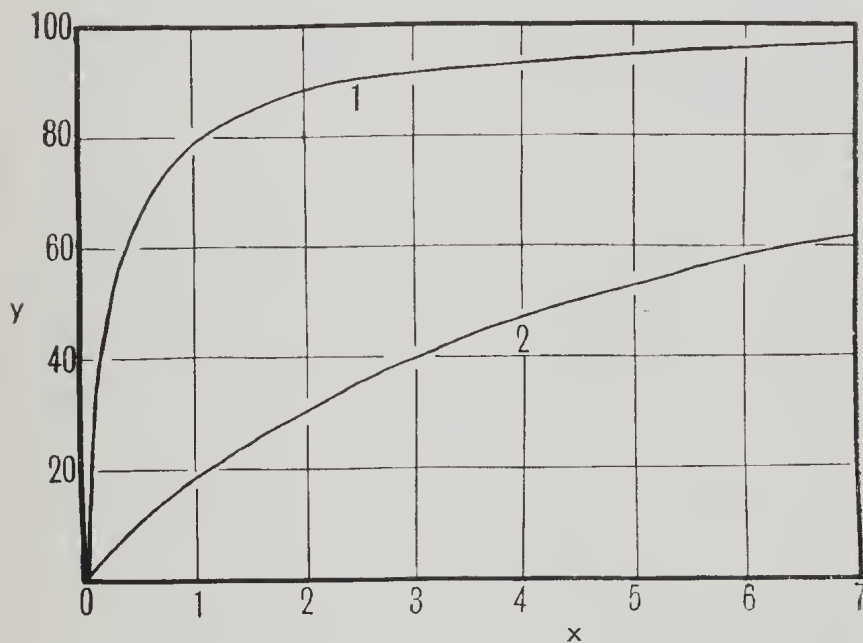


FIG. 2.

FIG. 2.—Curves to illustrate rate of liberation of exchangeable manganese from two types of soil, after Steenbjerg (1933). Curve 1, Soil No. 685, pH = 5.3.  $qS = 0.256$ ; Curve 2, Soil No. 1011, pH = 7.6,  $qS = 4.39$ . Each curve corresponds to the equation  $y(x + qS) = 100x$ .

The soil, after liming, contains small amounts of Mn exchangeable at pH 7, together with very variable amounts of  $\text{MnO}_2$  soluble in quinol at pH 7. The very small amounts of exchangeable Mn may perhaps delay the onset of deficiency disease for a few years; Clausen (1931), for instance, states that in Holstein the maximum effects are shown six years after overliming, and a similar position apparently holds for the University soil, since when the original, acidic soil was treated with lime, pot tests with oats showed manganese deficiency only in the



second year after heavy overliming. This delayed effect may also be connected with the slow process of oxidation, by atmospheric oxygen or by bacteria, by which basic manganous compounds are turned to  $MnO_2$ .

The  $MnO_2$  formed from  $Mn^{++}$ , after liming to over pH 7, is probably of the most actively oxidizing kind, but it is possible that in some circumstances it gradually "ages" and becomes less available. Though the active  $MnO_2$  is held to be available, it is definitely inferior to the bivalent form as a source of plant food; so that while a soil may before liming be perfectly healthy with 10 p.p.m. of Mn exchangeable at pH 7, and no reserve of active  $MnO_2$ , it will no longer be healthy after liming when much of the exchangeable Mn is converted into  $MnO_2$ . The healthy alkaline soils tested here both contain well over 100 p.p.m. of active "dioxide" Mn.

Lack of available manganese exists naturally on both light (e.g., Mt. Gambier) and heavy soils (e.g., Penola), while after liming it seems to occur almost entirely on sandy podzols, which may sometimes be rich in organic matter. The University soil is related to the limed podzols on the one hand and to the Mt. Gambier soil on the other. The deficiency of the University and the Mt. Gambier soils appears to be connected with their extreme immaturity. Possibly a waterlogging, unaccompanied by leaching, occurring even once in many years, would cure both of these soils.

Where the deficiency occurs naturally on heavy soils liable to waterlogging, as at Penola and in North Carolina (Willis, 1932), it is probable that the active  $MnO_2$  as soon as it is formed, is continually reduced and washed out; at Penola the *total* Mn is also very low. The acid podzols, on the other hand, lose their active  $MnO_2$  by reduction at low pH, followed by leaching; there is less need at low pH values to have the assistance of waterlogging to effect this change. The rapidity with which soluble Mn accumulates in some acid soils under optimum conditions, described by McCool (1934), illustrates this point.

It is suggested that about 25 p.p.m. of manganese soluble in ammonium acetate + 0.2 per cent. quinol at pH 7.0 is a safety limit for heavy liming. It is of course essential to test many more soils before such a figure can be accepted. The number of cases of deficiency following overliming in Australia is as yet one (here described) or perhaps two (see Bellarine, below), so that such tests would need to be made on soils in the podzol belt of the United States of America or of north-western Europe. Up to the present, however, liming has not been carried on to any great extent in the podzol belt of Victoria; and the figures of the Mn replaced by ammonium acetate at pH 7.0, with and without quinol, given in Table XI., refer to some typical southern soils.

TABLE XI.—AMOUNTS OF MANGANESE DISSOLVED AT pH 7.0 FROM PODZOLIC SOILS OF SOUTHERN VICTORIA.

	University.	Timboon.	Bellarine.	Coleraine.	Dixie.	Larrent.	Yarragon.
Ammonium acetate	15	0.2	5	7	21	98	100
"    + 0.2 per cent. quinol	0	0.7	3	10	33	127	285
pH of soil ..	5.0	5.6	5.4	6.1	5.5	5.8	5.5

Of the four soils low in available manganese, the University soil showed a deficiency some years after overliming, while the Bellarine soil has shown, in a heavily-limed patch, symptoms believed to be those of manganese deficiency. Pot tests are in progress to determine whether the other two soils of these four are liable to develop deficiency on heavy liming. If the surface soil is shallow, it is of course possible that the subsoil might avert deficiency in the field.

It might incidentally be pointed out that manganese deficiency cannot possibly be due to excess calcium ion concentration (cf. Lundegårdh, 1931, p. 219). The well sulphured University plots, on which not a sign of manganese deficiency was seen, had a higher concentration of calcium in solution (as calcium sulphate) than the alkaline plots, where the most soluble compound would be the bicarbonate. This higher concentration of the highly flocculating calcium ion on the acidic plots was shown by the very rapid flocculation of the soil after shaking with water.

### Note on the Availability of Iron.

Plants growing on certain calcareous soils are liable to a chlorosis which may be overcome by treatment with iron salts. As manganese and iron are both essential to plants, and are chemically alike in many ways, it might be expected that the availability of iron in the soil would be similar to that of manganese. Each metal forms well-marked bivalent "ous" compounds, from which a hydroxide or basic salt may be precipitated about pH 7, and in each case this precipitate is easily changed at atmospheric oxygen to the "ic" state, corresponding to an extremely weak base. Again, deficiency is noted almost exclusively on soils on the alkaline side of neutrality, and may be overcome by treating the plant or the soil with a soluble "ous" salt, usually the sulphate. The bivalent state in the soil may also be reached in each case by reducing conditions such as waterlogging.

Ferrous hydroxide is both a weaker base than manganous hydroxide, and more easily oxidized. Halvorson (1931) estimated the concentration of ferrous ion in solutions of  $\text{FeSO}_4$  of

varying pH values exposed to the atmosphere for four months, and expressed his results by the formula—

$$[\text{Fe}^{++}] [\text{OH}^-]^2 = 4.8 \times 10^{-25},$$

where any attempt to increase the ferrous ion concentration at a given pH would lead to the deposition of ferric hydroxide. He also used the solubility product of  $\text{Fe}(\text{OH})_3$ , the potential values of the ferric-ferrous electrode and the oxygen-hydroxide electrode to calculate the *theoretical* value of the above expression, namely—

$$[\text{Fe}^{++}] [\text{OH}^-]^2 = 3.7 \times 10^{-31}.$$

The difference between these two values is due to the slowness of the reaction. But each equation shows that the concentration of ferrous ion in solution in a well-aerated soil must be very low. While information is lacking as to the quantities of exchangeable  $\text{Fe}^{++}$  to be expected in soils, it has been pointed out by Afanassiev (1930), and by Morison and Doyne (1914), that the ferrous ion found in solutions extracted from soil by acids is due to the reduction of ferric compounds by organic matter at low pH values at which ferric compounds are more soluble, and hence strong oxidizing agents. Manganous ions are liberated at low pH values by an analogous reaction from manganic compounds.

Both ferric and manganic ions may be ruled right out of consideration as a source of food for plants above pH 6. The only other possibilities remaining are the absorption of these elements as complex ions, and the use of colloidal ferric or manganic compounds, as suggested above, directly, or by reduction at the root-soil interface. It is the former possibility that marks off iron from manganese. Manganic complexes certainly exist, but they are neither stable nor well-defined, while trivalent iron forms complexes, which are soluble at high pH values, with several hydroxy-acids, such as citric and tartaric acids. (It need hardly be pointed out that the ferric ion concentration at pH 7 is *lower* in the presence of citrate than in its absence.) It seems very likely that such "ferri-organic" complexes are the source of the high intake of iron by plants growing on peaty soils after heavy liming. Olsen (1930) has remarked that comparing soils of the same pH value, chlorosis is more likely to occur on soils poor in organic matter—a fact which he attributes to ferri-organic complexes, a far more likely explanation than the common one that the organic matter reduces the iron to the ferrous state, which is hard to accomplish in the presence of oxygen at such high levels of pH.

On account of these ferri-organic complexes, the actual content of iron in even highly chlorotic plants growing on calcareous soil may be of the same order as in healthy plants. (It may even be higher, which may be connected with the high stability of

ferri-organic complexes at pH 7.) As these chlorotic plants readily respond to sprays or injections of ferrous sulphate or ferric citrate, it is clear that this chlorosis is due to immobility of the iron, i.e., a physiological disturbance; and Rogers and Shive (1932) have suggested that it is due to the failure of the affected plants, which all have a sap of high pH, to produce, or conserve, the hydroxy-acids needed to keep the iron in the sap soluble and mobile; and such a failure is associated especially with certain calcareous soils, and also with manganiferous, non-calcareous soils in the pineapple-growing regions of Oahu.

If, as has at times been suggested, the actual *intake* of iron from manganiferous soils is too low for healthy growth, it is conceivable that the following reason may hold: If iron can also be absorbed by the reduction of ferric colloids at the root-soil interface, a low rH must be reached (at the higher pH values) to achieve this; and this lowering of rH cannot be achieved so long as active manganic compounds are present. This, in fact, is implied by Willis (1932), who, however, was more concerned with the *oxidation* of iron and manganese. Since all the iron and nearly all the manganese will in any case be in the more oxidized form in a well-aerated, neutral soil, it seems more helpful to focus attention rather on the possibility of *reduction* by the root. However, it is possible that the suggestion dealt with in this paragraph is superfluous.

Large amounts of iron were liberated by some of the treatments described in this paper, but no analyses were carried out.

It might be pointed out here—perhaps a fact of practical significance—that apparently no soil has yet been reported on which *both* iron and manganese deficiency exist.

### Summary.

Wheat plants growing on a heavily limed soil have been found to suffer from lack of available manganese. This state of things was improved either (1) by acidification of the soil, most conveniently by sulphur, to a pH at least as acid as 6.5, or (2) by heavy applications of manganous sulphate to the soil.

The first treatment had no effect on early growth, nor on the number of tillers produced in late September, but it led to a far higher survival of tillers to grain-bearing ears, and an increase in the number of grains per ear, and in the weight per grain.

Powdered manganese sulphate had no effect when applied to the soil at the rate of 40 lb. of the crystals per acre, whether at germination or in the spring. The best response was obtained by applying 1 cwt. per acre, sown with the seed, or applied to the soil at germination, and a residual effect was noted a year later. The application of 1 cwt. increased the tillering, especially when applied with the seed, and also improved the survival rate of the tillers and the weight of grain per ear compared with the



control plots, but the  $\text{MnSO}_4$  plots were very inferior to the sulphured plots in these last two values, so that the final yield of grain averaged the best on the sulphured soil.

It is possible that the poorer survival on the  $\text{MnSO}_4$  plots was due partly to the too great tillering of the plants, leading to a loss in the warm, dry weather of late spring. In any case, the experiments definitely show that, if the production of grain is the aim, the more effective way of dealing with overliming, in the Melbourne climate at least, is to bring the pH down again by the use of heavy applications of sulphur, possibly in more than one annual instalment. It is, however, possible that results might have been different if the  $\text{MnSO}_4$  had been thoroughly worked into the soil.

Laboratory tests on various soils have shown that the crucial test among soils of pH greater than 7 is to leach the soil with a solution of quinol at pH 7 (normal ammonium acetate was the reagent used). Deficient soils yielded less than 15 parts of Mn per million of soil to this solution, while two typical healthy soils tested gave over 130 parts per million.

The theory of this test is discussed in connexion with the oxidation-reduction potential of the system ( $\text{MnO}_2 - \text{H}^+ - \text{Mn}^{++}$ ). It is suggested that the plant uses  $\text{MnO}_2$  as its source of manganese, whether directly in the colloidal state or by reduction at the root-soil interface, and it is only the manganese dioxide dissolved by quinol at pH 7 which can be used by plants, and not the more copious supply that may sometimes be dissolved with or without quinol at low pH value (1 to 2). The magnitude of this figure (Mn dissolved by quinol at pH 7) may be taken as a test whether a given soil is liable to develop manganese deficiency after liming, though this suggestion can hardly be tested in this country, where no important areas have suffered from overliming.

If sulphuring is impracticable (as it will be on a very calcareous soil) an "active"  $\text{MnO}_2$  should on theoretical grounds be as good as  $\text{MnSO}_4$ , especially if finely divided and worked well into the soil.

It is suggested that information may be gathered as to the state and translocation of manganese in the soil by leaching with a series of solutions buffered to a constant pH and poised to steady ranges of rH by a series of materials such as quinol.

### Acknowledgments.

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## Appendix.

## Method of Analyzing for Manganese.

Manganese was analyzed colorimetrically as the permanganate in all the above work, using a Dubosq colorimeter. The colour was developed by sodium periodate, usually in sulphuric acid solution, but sometimes in phosphoric acid solution if it was necessary to avoid the formation of large amounts of calcium sulphate. The plant ash material was treated with hydrofluoric acid to avoid loss of manganese as insoluble silicate, the hydrofluoric acid being then destroyed with sulphuric acid. The ammonium acetate solutions were treated by first evaporating them to small bulk, then destroying organic matter and ammonium ions with aqua regia, finally destroying chlorides by treating with sulphuric or phosphoric acid.

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## SUPPLEMENTARY NOTE.

Pot tests carried out in the open since this paper was read have confirmed the above evidence that plants can use "active"  $MnO_2$ . One pot (A) contained 25 kg. of a typical "deficient" soil from Mount Gambier, which before being placed in the pot was thoroughly and uniformly mixed with a freshly prepared sample of  $MnO_2$  containing 2 gm. manganese (or 80 parts of Mn per million of soil). This  $MnO_2$  was made by mixing strong solutions of  $NaMnO_4$  and  $MnSO_4$ , filtering the brown precipitate and washing it several times with dilute  $H_2SO_4$ , then with dilute  $NaOH$ , finally with water. The control pot (B) contained 25 kg. of the same deficient soil. Two grams each of superphosphate and sodium nitrate were applied to the surface of each pot, and 0.25 gm.  $MnSO_4$  crystals was added at the same time uniformly to the surface of pot B. Six seedlings of a variety of Tasmanian White Oats (known to be sensitive to deficiency) were transplanted to each pot on 10th October, 1934, when all were in the one-leaf stage. Temperatures were normal during the next two months, and 13 inches of rain fell. Differences in growth appeared early in the experiment, and by 6th December the oats on pot A had tillered vigorously and were free from any sign of deficiency, while marked symptoms of "grey speck" were shown by the plants on pot B, which had made only poor growth. This clearly supports the suggestion that the failure of surface applications of manganese salts is due to "positional" unavailability, which may be overcome by thorough mixing. It also makes it more reasonable to expect that large applications of  $MnSO_4$  will bring about a permanent cure on any soil, if thorough mixing is possible.